

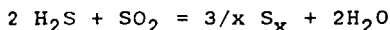
# The Kinetics of the Reaction of Hydrogen Sulfide and Sulfur Dioxide in Organic Solvents

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## I. Introduction

Hydrogen sulfide is an undesirable component found in many industrial process streams. Traditionally its removal and recovery have been accomplished in an absorber-stripper operation, followed by the Claus process in which the  $\text{H}_2\text{S}$  is reacted over alumina catalyst with  $\text{SO}_2$  obtained by burning a portion of the inlet stream. The gas-phase reaction to produce sulfur is



This reaction is equilibrium-limited to 95 to 97% conversion in 2 to 4 stages because the temperature must be kept above the dewpoint of sulfur. Additional processing must be provided to reduce the concentration of sulfurous compounds in the effluent to environmentally acceptable levels.

When the reaction between  $\text{H}_2\text{S}$  and  $\text{SO}_2$  is carried out in organic liquids at temperatures below  $150^\circ\text{C}$  it is irreversible and goes essentially to completion. In many organic solvents, such as triethylene glycol, dimethyl ether (Triglyme) and diethylene glycol, methyl ether (DGM), the reaction is impractically slow and, at room temperature, the sulfur formed is too finely divided to be readily separated. Urban (3) found that the presence of N,N-dimethyl aniline (DMA) increased the crystal size of the precipitated sulfur. Furthermore, DMA accelerates the reaction to the extent that 99+% removal of  $\text{H}_2\text{S}$  is possible with careful selection of the solvent mixture.

The present work was undertaken to study the reaction between  $\text{H}_2\text{S}$  and  $\text{SO}_2$  in mixtures of DMA/Triglyme and DMA/DGM. Experiments performed by monitoring the temperature rise of this exothermic reaction in an adiabatic calorimeter show the effects of various solvent compositions on the kinetics of the reaction. Solvent selection criteria for an appropriate process scheme can then be set. This reaction system is suitable for application to a process currently being studied in this laboratory for the removal of hydrogen sulfide from industrial gas streams.

## II. Experimental Methods

All rate measurements were made in a 50-ml Erlenmeyer flask that contained a magnetic stir bar and was sealed by a septum cap (see Figure 1). Insulation was provided by a styrofoam block with a hole drilled out for the reactor. Reaction progress was monitored by recording the temperature rise in the form of a millivolt potential produced by a bare, type J thermocouple connected to a chart recorder. A measured quantity of a solution of one reactant was first placed in the reaction vessel. The reaction was initiated when a measured quantity of a solution of

the second reactant at the same temperature was injected quickly into the stirred vessel by syringe.

### III. Methods of Analysis

#### A. Acid-Base Experiments

Reactions between NaOH and HCl were carried out in the calorimeter to determine the rate of mixing, the thermal mass of the apparatus, and the rate of heat loss from the system. The experimental method was that used in the H<sub>2</sub>S-SO<sub>2</sub> reactions and the quantities of reactants used gave similar temperature rises. Since the acid-base reaction is practically instantaneous, the time necessary for completion is the mixing time.

A heat balance applied to the apparatus and solution allows calculation of the thermal mass of the reactor. Furthermore, by measuring the decrease in temperature with time after the initial rise, the rate of heat loss from the system can be determined.

A chart recorder trace of thermocouple potential (i.e., temperature) versus time for an acid-base reaction is shown in Fig. 2. The estimated heat leakage from the reaction vessel and styrofoam block corresponds to a rate of temperature loss that is less than 0.002 °C/sec. Thus, there was a loss of about 0.02 °C over the course of a typical H<sub>2</sub>S - SO<sub>2</sub> run. Since in the majority of experiments the temperature rise is 5 °C or less, this amounts to an uncertainty of about 0.4% in the maximum temperature.

The average value of  $t_{mix}$  is approximately 0.7 sec for the solution volumes of acid and base and stirrer speeds used in these experiments. Presumably, in cases where the reaction between H<sub>2</sub>S and SO<sub>2</sub> takes longer than this period, the reaction is then occurring in a homogeneous solution.

From the known heat of reaction for  $H^+ + OH^- (= -13.4 \text{ kcal/mole of } H_2O \text{ formed})$  and the heat capacity of the aqueous solutions (approximated as water,  $C_p = 1 \text{ Cal/g } ^\circ\text{C}$ ), the thermal mass of the apparatus was determined to be 0.6 cal/°C. Since in these experiments the thermal mass of the solution for a typical run was 12-15 cal/°C., the contribution of the apparatus to the total heat capacity of the system was small.

#### B. Kinetics

If the reaction between H<sub>2</sub>S and SO<sub>2</sub> is first order in both reactants, then the differential rate equation for the disappearance of SO<sub>2</sub> or H<sub>2</sub>S is

$$-dC_A/dt = -1/2 dC_B/dt = k_2 C_A C_B \quad 1)$$

By stoichiometry

$$C_B = C_B^0 - 2(C_A^0 - C_A) \quad 2)$$

in which the superscript 0 refers to time = 0. Substituting Eq. 2 into Eq. 1 and rearranging yields the following rate expression:

$$k_2 dt = dC_A / (C_A^* (2C_A - 2C_A^0 + C_B^0)) \quad 3)$$

Integration of Eq. 3 and simplification gives

$$k_2 t = (1/(2C_A^0 - C_B^0)) \ln ((C_B^0/C_A^0) * (C_A/C_B)) \quad 4)$$

If a reaction is first order with respect to both A and B then a plot of the integrated rate expression on the right-hand side of Eq. 4 versus time should lie on a straight line with a slope of  $k_2$ . Note that when the initial concentrations of  $H_2S$  and  $SO_2$  are stoichiometrically equivalent, Eq. 4 reduces to the more familiar second-order relationship

$$k_2 t = 1/C_A^0 - 1/C_A^0 \quad 5)$$

Equation 4 is in the form of concentration and time whereas the quantities measured experimentally are temperature and time. If the temperature rise for the exothermic reaction between  $H_2S$  and  $SO_2$  is assumed to be proportional to the extent of reaction (i.e. is a measure of reaction progress) and if the maximum temperature corresponds to complete reaction (fraction conversion = 1.0) with any uncertainty arising from thermal losses, then for any time  $t < t_{max}$  the concentration of the limiting component is related to the temperature rise by the expression

$$C = C^0 * (1 - \Delta T / \Delta T_m) \quad 6)$$

From this concentration and the known stoichiometry, the concentration of the other reactant can be calculated. In order to keep the uncertainty arising from thermal losses to a minimum, only temperature rises less than 90% of the maximum value are used for determining reaction-rate constants.

In the preceding analysis perfect mixing has been assumed. Since these experiments require the injection of one of the reactant solutions into the other, a finite period, whose length depends on the sample volumes, solvent viscosity, and stirrer speed, is needed to completely mix the components. Before mixing is complete, local inhomogeneities exist in which one of the reactants is in large excess. The other reactant is rapidly depleted, effectively reducing the reaction rate in these regions to zero. Overall, the experimentally measured rate is lowered and the kinetics of the reaction under such conditions is of uncertain significance. Once the solutions are thoroughly mixed, the rate becomes that for the homogeneous reaction. The rate constant can be determined from plots of the integrated rate expression (Eq. 4) versus time by considering only the portion of the plot for which the time is greater than the mixing time.

### C. Heat of Reaction

The heat of reaction for each of the experiments is calculated from the measured temperature rise and the thermal properties of the system. An enthalpy balance yields

$$\Delta H_{rxn} = ((mC_p)_s + (mC_p)_{app} \Delta T) / 1000 n_L \quad 7)$$

The heat capacity of the organic solution, which was assumed to include all solvents and products, was estimated by a group contribution method applied to the bulk solvent used in a given run. Calculations for Triglyme and DGM using Missenard's group contribution method (2) give a value of  $C_p \sim 0.5 \text{ cal/g-}^\circ\text{C}$ .

#### IV. Results and Discussion

##### A. Results for the Reaction of $\text{H}_2\text{S}$ and $\text{SO}_2$ in Triglyme/DMA/ $\text{H}_2\text{O}$

Kinetic data were analyzed using equation Eq. 4. Plots of the concentration expression on the right side of Eq. 4 versus time yield a straight line (in the region  $t > t_{\text{mix}}$ ) with a slope of value  $k_2$  when the reaction follows second-order kinetics. Data pairs of potential/time obtained from the chart-recorder traces were converted into concentration/time pairs and plotted in the integrated rate form.

A sample plot for the reaction of  $\text{H}_2\text{S}$  and  $\text{SO}_2$  in a DMA/Triglyme mixture is shown in Fig. 3. Values of  $k_2$  were obtained from similar plots by drawing the best straight line through the data. The curvature at times less than 1 sec. results from the finite time required for injecting the  $\text{SO}_2$  sample and mixing the solution. In nearly all of the runs the time intercept, as found by extrapolating the line drawn through the integrated rate data back to the time axis, is about 0.5 to 0.8 seconds. These values, which approximate the mixing time in the  $\text{HCl} - \text{NaOH}$  experiments, show little variation from run to run and thereby indicate a high degree of reproducibility in the experimental conditions and technique. Furthermore, since this result agrees with the mixing time obtained in the acid-base experiments, data points at longer times presumably represent the progress of the reaction in a well-mixed solution.

Most of the experiments presented here were performed with nearly stoichiometric equivalents of  $\text{H}_2\text{S}$  and  $\text{SO}_2$ . Additional experiments were carried out with the ratio of  $\text{H}_2\text{S}$  to  $\text{SO}_2$  varying from about 2:1 to 1:2. In all cases the second-order rate expression provided the best straight line fit to the data in spite of a four-fold change in  $\text{SO}_2$  concentration. Attempts to analyze the data using a rate expression which is second order in  $\text{H}_2\text{S}$  and first order in  $\text{SO}_2$  yielded non-linear integrated rate plots.

The results for the reaction in Triglyme with DMA and water present are summarized in Fig. 4, where the second-order rate constant is plotted as a function of wt% DMA for various  $\text{H}_2\text{O}$  concentrations. With pure Triglyme as the sole solvent, plots of the integrated rate expression versus time are non-linear, increasing in slope as time progresses. Tangents to these curves correspond to  $k_2$  values of 0.5 lit/mole-s or lower. The curvature, which reflects an increase of the rate constant with time, may be due to an autocatalytic effect of water formed during the reaction or possibly to a change in the reaction mechanism. Note that while a mixture of water/Triglyme speeds the reaction, it is unclear whether the same reaction pathway is followed since some of the integrated rate plots are non-linear. Perhaps other products such as sulfoxy acids, which frequently form in aqueous media, are being created in these cases.

When DMA is added to Triglyme, the integrated rate plots become linear, i.e. there is a first - order dependence on both  $\text{H}_2\text{S}$  and  $\text{SO}_2$ . Furthermore, there is a substantial increase in the rate when DMA is added to the Triglyme. Addition of only 2 wt% DMA more than doubles the reaction rate over that observed for Triglyme alone. Increasing the DMA concentration increases the rate constant,  $k_2$ , which asymptotically approaches a value of 8 lit/mole-s.

The presence of water in DMA/Triglyme greatly accelerates the rate as evidenced in Fig.4. Addition of 4 to 5 wt%  $H_2O$  doubles the observed rate constant. Also, the value of  $k_2$  for the mixed solvents exceeds the sum of those for the reaction carried out with only one of the catalysts (DMA or  $H_2O$ ) present. This suggests a synergism between the effects of the water and DMA.

#### B. Results for the Reaction in DMA/DGM/Water

The kinetic behavior of the reaction in DGM alone is similar to that observed for Triglyme. DGM has little or no catalytic effect, and plots of the integrated rate expression exhibit an increase in rate with time. However, values for  $k_2$  are considerably higher when a given wt% DMA is added to DGM than are those found in the Triglyme runs. The rate constants for the reaction of  $H_2S$  and  $SO_2$  in DMA/DGM mixtures are shown in Fig. 5. The DGM also seems to have a catalytic effect on the reaction; increasing the DMA percentage toward pure DMA causes a noticeable decrease in rate as opposed to the monotonic increase observed in Triglyme mixtures. The maximum value of  $k_2$ , which is approximately 20 lit/mole-s, is more than twice as large as that obtained in the Triglyme/DMA cases with no water present.

The addition of water to DMA/DGM mixtures has little or no effect on the rate, as is reflected in the data presented in Table 1. At 10 wt% DMA the rate constant has attained its maximum value and the addition of water does not increase the rate.

A few runs with 2.5 wt% DMA in DGM, performed at 7 to 10  $^{\circ}C$ , yielded an average  $k_2$  of 4.5 lit/mole-s (see Table 2). On the basis of these data and those in Fig. 5, the estimated activation energy is 7.4 kcal/mole, which corresponds to a doubling of the rate every 20  $^{\circ}C$ .

#### C. Results for the Reaction in DMA/Triglyme/Methanol

A reasonable hypothesis to explain the fact that both  $H_2O$  and DGM accelerate the reaction between  $H_2S$  and  $SO_2$  in the presence of DMA is that the hydroxyl group is exerting a positive catalytic effect. In order to further substantiate this idea, a few experiments were performed in which methanol was added to DMA/Triglyme. The data are summarized in Table 3. The presence of the indicated methanol concentration increased the rate constant by a factor of 6 over that for the same concentration of DMA alone in Triglyme. As in the DMA/Triglyme/Water runs, adding methanol to the mixture enhances the observed reaction rate. Also, the rate constant for this mixture, which contains an eight-to-one mole ratio of methanol to DMA, is about the same as the value of  $k_2$  for the same molar ratio of DGM to DMA. Thus, for cases in which the same ratio of hydroxyl groups to DMA is used, similar effects on the reaction kinetics might be expected.

#### D. Heat of Reaction

The heat of reaction between  $H_2S$  and  $SO_2$ , taken as the average for a large number of data points, is 28 to 29 kcal/mole of  $SO_2$  reacted. This value seems to apply equally well to all mixtures of the solvents used in these experiments. Evidently, effects such as heats of solution are small or similar in magnitude for the range of cases considered.

### E. Summary

From these experimental results it is readily apparent that the presence of DMA greatly accelerates the reaction of  $H_2S$  and  $SO_2$  in organic solvents. The nitrogen of the amine, which is noted for its ability to form complexes with sulfur dioxide (1), presumably provides a favorable site at which the reaction can occur. This effect seems to be dependent on the concentration of the catalytic agent rather than its ratio to either of the reacting components, since the mole ratio of DMA to  $SO_2$  exceeds one at less than 1 wt% DMA in most of the experiments. This suggests that the enhancement is related to the accessibility of sites rather than the actual number present. In the DMA/Triglyme experiments the rate constant increases with increasing DMA, implying that the Triglyme has little or no catalytic effect and actually reduces the rate by diluting the concentration of useful reaction sites.

For the reaction in DGM an additional factor is found to be important. The DGM appears to work with DMA in accelerating the reaction, producing a maximum rate when intermediate concentrations of both solvents are present. This enhancement seems to be related to a catalytic effect of the OH group of the DGM that is synergistic with DMA. Further evidence of the OH effect can be seen in the results for the reaction in DMA/Triglyme with water present; indeed this effect may be expected for alcohols in general since the experiments performed with DMA/ Triglyme/Methanol yielded similar results. Determination of whether the hydroxyl provides an alternate reaction site or speeds an intermediate or parallel step or causes some other enhancement will require further investigation. It is clear however, that mixtures of DMA with glycol mono ethers are good solvents for the catalysis of the reaction between  $H_2S$  and  $SO_2$  to form sulfur.

### Acknowledgement

This work was supported by the Morgantown Energy Technology Center, Assistant Secretary for Fossil Energy, Office of Coal Utilization, Advanced Research and Technology Development, Division of Surface Coal Gasification, through the US Department of Energy under Contract No. DE-AC03-76SF00098.

### References

1. Hill, Arthur E., and Thomas B. Fitzgerald, "The Compounds of Sulfur Dioxide with Various Amines," J. of Am. Chem. Soc., 57, 250 (1935).
2. Reid, Robert C. , John M. Prausnitz, and Thomas K. Sherwood, "The Properties of Gases and Liquids", McGraw-Hill, NY, (1977).
3. Urban, Peter, "Production of Sulfur," U.S. Patent #2,987,379 (June 1961).

# Notation

$C_A, C_B$	= Concentration of $SO_2$ and $H_2S$ at time $t$ (mole/lit)
$C_A^0, C_B^0$	= Concentration of $SO_2$ and $H_2S$ at time 0 (mole/lit)
$\Delta H_{rxn}$	= Heat of reaction (kcal/mole)
$k_2$	= Second-Order Rate Constant (lit/mole-s)
$(mC_p)_s$	= Thermal mass of solution (cal/°C)
$(mC_p)_{app}$	= Thermal mass of apparatus (cal/°C)
$n_L$	= Moles of limiting reactant
$t$	= time (sec)
$\Delta T, \Delta T_m$	= Temp. change and maximum temp. change (°C)

Table 1  
Rate Constants for the Reaction of  $H_2S$  and  $SO_2$  in  
DMA/DGM with Water Added

Wt% $H_2O$	Wt% DMA	$k_2$ (lit/mole-s)
0.5	9.8	20.4
0.5	9.8	21.6
1.4	9.7	22.8
1.6	9.7	22.1
2.4	9.6	21.3
2.6	9.6	23.5

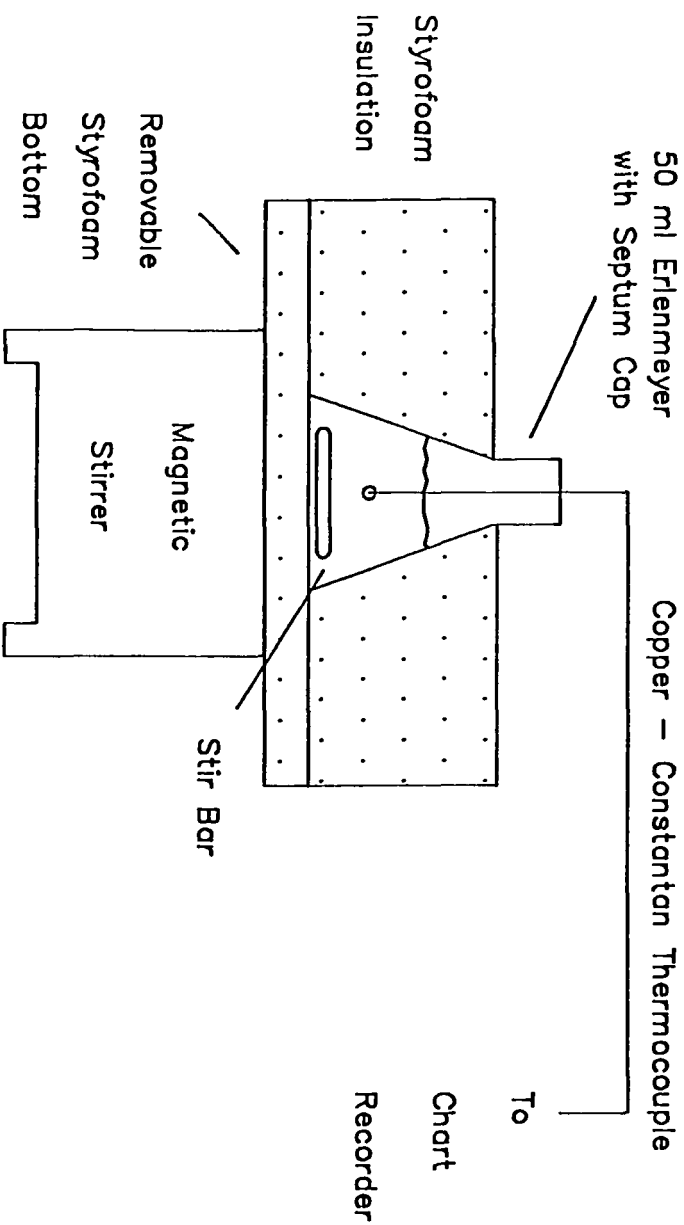
Table 2  
Rate Constants for the Reaction Between  $H_2S$  and  $SO_2$  in  
2.5 Wt% DMA in DGM at 7-10 °C

RUN	$k_2$ (lit/mole-s)
1	2.5
2	4.3
3	5.0
4	4.3

Table 3  
Rate Constants for the Reaction of  $H_2S$  and  $SO_2$  in  
DMA/Triglyme/Methanol Mixtures

RUN	Wt% DMA	WT% Methanol	$k_2$ (lit/mole-s)
1	10.1	45.1	23.5
2	10.1	45.2	24.0
3	10.1	45.1	22.8

Figure 1  
Experimental Apparatus





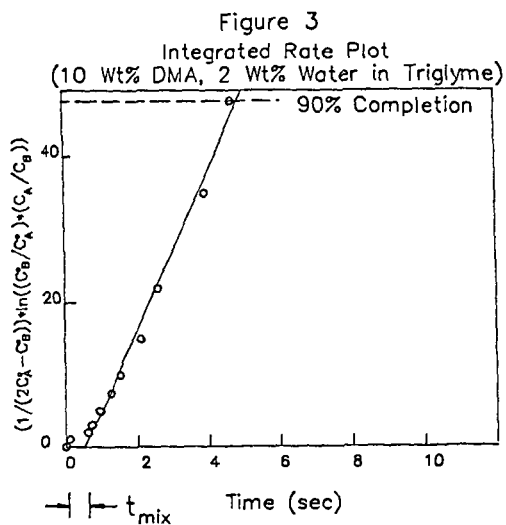
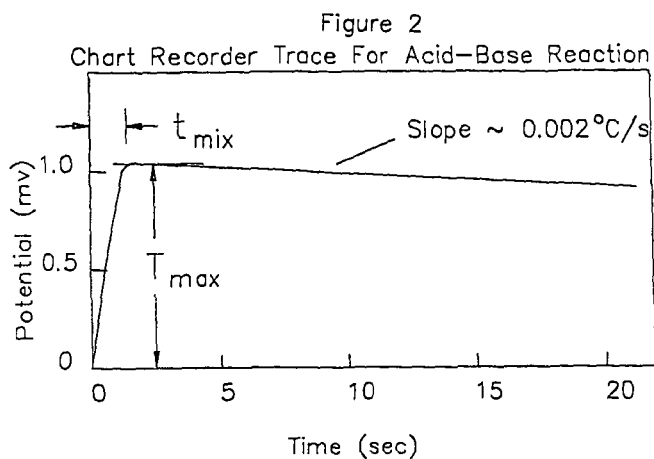


Figure 4

Variation of Second-Order Rate Constant  
with DMA and Water Content for the Reaction  
of Hydrogen Sulfide and Sulfur Dioxide in Triglyme

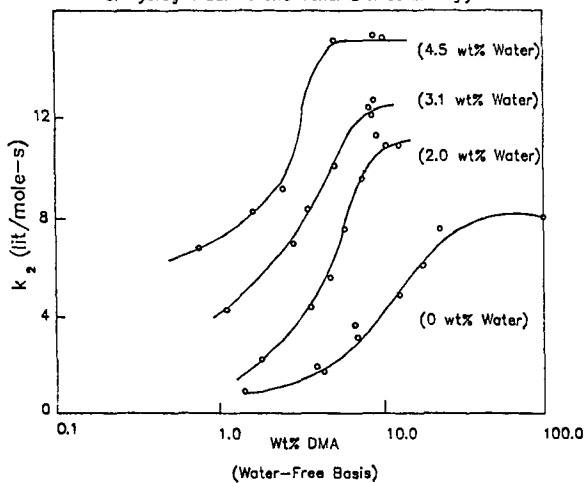


Figure 5

Variation of Second-Order Rate Constant with Wt% DMA  
For DMA in DGM at 17-23°C (No Water)

